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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process for the production of Chloramine

We, W. R. GRACE & CO., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 7, Hanover Square, New York 5, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for forming chloramine by the reaction of ammonia and chlorine.

It is known that chlorine and ammonia may be reacted to form chloramine according to the following equation:

$$2NH_3 + Cl_2 \rightarrow NH_2Cl + NH_4Cl$$

Since the reaction is exothermic, elevated temperatures of from about 100° C. to about 150° C., have generally been employed for the reaction. At such temperatures, the formation of ammonium chloride is proportionally quite high and an accumulation of ammonium chloride in the reactor generally requires a shut down at frequent intervals for cleaning. Also, in order to obtain yields of about 80% or more the mode ratio of ammonia to chlorine was required to be in excess of 11. It has now been found that by modifying the reaction conditions and mole ratios, excellent yields may be obtained without the fouling of the reactor with ammonium chloride.

Accordingly, it is an object of the present invention to provide a continuous process for the manufacture of chloramine which gives chloramine in high yields and/or with little or no fouling of the reactor.

According to the present invention there is provided a process for forming chloramine which comprises continuously reacting in the gaseous phase one molar proportion of chlorine with at least 1.9 molar proportions of ammonia in the presence of at least 1 molar proportion of an inert diluent gas at a temperature of at least 250° C. A suitable inert diluent gas is nitrogen, and in the examples which follow nitrogen is used because it is cheap, safe and readily available. Clearly however a vast range of alternative diluents is available which are inert under the reaction conditions and do not interfere with the reaction. A suitable diluent will be chosen according to working conditions.

In a preferred embodiment of the present invention the ammonia to chlorine is maintained at from 2 to 15, better to about 10, more preferably 2 to 5. In the preferred embodiment, the reaction is carried out at a temperature of from about 275° C. to about 700° C., preferably from about 290° C. to about 350° C.

In a still more preferred embodiment of the present invention, the gaseous reaction products are maintained at a temperature of from about 50 to about 250° C. until at least a portion of the ammonium chloride is solidified. The ammonium chloride solids are removed, preferably while the reactants are maintained at the reaction temperature, and thereafter the gaseous chloramine is recovered, preferably in a solvent, e.g. diethyl ether.

In reacting the gaseous components, it is preferred that the ammonia and nitrogen be mixed and the chlorine fed into the mixture at substantially atmospheric pressure. This procedure allows the reaction to be easily controlled particularly when used with the reactor shown in the drawings. However, lower or higher pressures may also be used if desired.

A suitable technique for carrying out the invention will now be described with reference to the accompanying drawing of the apparatus used.

In carrying out the following examples the reactor described in the drawing was utilized. For convenience, many parts of the reactor are labelled rather than numbered. The

reactor consists of three zones, an entrance zone 8, a reaction zone 9 and a cooling zone 10. Ammonia is admitted to the entrance zone through a port in the side thereof and the inert gas usually nitrogen is mixed with the ammonia from a tube which projects downwardly from the top of the entrance zone. The nitrogen tube is concentric with and surrounds another tube through which chlorine is supplied. The chlorine tube projects below the end of the nitrogen tube and is downwardly tapered so as to deliver a jet of chlorine into the nitrogen-ammonia mixture. The point of entry of chlorine into the reaction zone may be adjusted by an adjustable sleeve (labelled). Both chlorine and nitrogen in the top assembly are heated by means of an electric heater (labelled) to a temperature approximating the reaction temperature. The temperature is measured by a thermocouple (labelled). The nitrogen gas is brought into an entrance zone in the left side of the assembly by means of a port (labelled). The entrance zone 8 and the reaction zone 9 consist of an inner quartz lining 1 which is wound with an insulated heating tape 2 which is then covered by conventional insulation 3. A thermocouple (labelled) is used to observe the temperature within the inner quartz lining 1. By regulating the amount of current through the heating tape 2, the temperature within the reaction zone can be varied as desired. The cooling zone 10 consists of an inner "Pyrex" glass liner 4 ("Pyrex" is a Registered Trade Mark) which is surrounded by a cylindrical metal holder 5. The cylindrical metal holder 5 is wrapped with a heating tape 6 which is covered by insulation 7. At the bottom of the cooling zone 10, glass wool (labelled) is inserted. In actual practice, the entrance zone 8 and reaction zone 9 are kept at the reaction temperature. In cooling zone 10, however, the temperature is maintained at a value somewhere between 50° C. and 250° C. to solidify the ammonium chloride which collects on the glass wool. The chloramine then proceeds out of the cooling zone where it collected in the solvent diethyl ether. In the examples, the cooling zone is maintained at a temperature of about 75° C. The chloramine is analysed by a conventional procedure from the diethyl ether solution.

Examples 1 to 6

The above described reactor is employed to form chloramine under the conditions given below. In the actual reactor employed, the widest portion of the entrance zone is approximately 50 millimetres in diameter, the entrance zone plus the reaction zone is about 10" in length, the chlorine entrance tube has a diameter of about ½ millimetre the concentric inert gas tube (in this case nitrogen) has a diameter of about 2 millimetres and the total length of the cooling tube is approximately 15". The mole ratios and temperature are given in the table below.

Reaction of Cl_2 and NH_3

Experiment No.	$Cl_2/NH_3/N_2$ Mole Ratio	Moles Cl_2/min.	Temp. of Cooling Zone (glass wool)	Temp. of Entrance Zone and Reaction Zone	Yield of NH_2Cl, %
1	1/2.04/12.73	1.02	75°C.	300°C.	94
2	1/2.10/8.00	1.00	75°C.	300°C.	90
3	1/2.10/3.29	0.86	75°C.	300°C.	89
4	1/13.2/2.49	0.93	75°C.	300°C.	87
5	1/2.06/11.19	0.95	75°C.	300°C.	94
6	1/3.48/12.80	0.789	75°C.	300°C.	91

Examples 7 and 8

The procedure of Example 1 is repeated keeping all conditions the same with the exception that the reaction zone employs a temperature of 475° C. in one case and 600° C. in the second case. Substantially the same yields are obtained as in Example 1.

While in the above examples nitrogen is employed as the inert diluent gas, any gas may be employed which does not react with the components in the reactor. For example, argon, neon, carbon dioxide, helium, krypton as well as other gases may be used in place of the nitrogen. Also, solvents other than

diethyl ether may be used to collect the chloramine. For example, toluene, benzene, a chlorobenzene may also be employed.

WHAT WE CLAIM IS :

1. A process for forming chloramine which comprises continuously reacting in the gaseous phase one molar proportion of chlorine with at least 1.9 molar proportions of ammonia in the presence of at least 1 molar proportion of an inert diluent gas at a temperature of at least 250° C.

2. The process of claim 1 wherein the molar proportion of ammonia to chlorine is from 2 to 15.

3. The process of claim 1 wherein the molar proportion of ammonia to chlorine is from 2 to 5.

4. The process of claim 1 wherein the reaction is carried out at a temperature of from about 275° C. to about 700° C.

5. The process of claim 1 wherein the reaction is carried out at a temperature of from about 290° C. to about 350° C.

6. A process according to any preceding claim in which the reaction products are maintained at a temperature of from about 50° C. to about 250° C. while the solid ammonium chloride which forms is removed.

7. A process according to any preceding claim in which the gaseous chloramine product is recovered in a solvent.

8. A process according to claim 7 in which diethyl ether is used as the solvent.

9. A process according to any preceding claim in which a mixture of the ammonia and the diluent gas is first formed, and then chlorine is fed into the mixture.

10. A process according to any preceding claim in which nitrogen is used as the diluent.

11. A process for the preparation of chloramine according to claim 1 and substantially as hereinbefore described.

12. A process for the preparation of chloramine substantially as hereinbefore described with reference to the accompanying drawing.

13. Chloramine produced by a process according to any preceding claim.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*